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MINISTRY OF ENVIRONMENT, LANDS AND
PARKS

Ambient Water Quality Guidelines for Manganese

OVERVIEW

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SUMMARY

THIS DOCUMENT is one in a series that establishes ambient water quality guidelines for British Columbia (Table 1). It is primarily based on the thesis submitted by P. S. Reimer, Department of Chemical and Bio-Resource Engineering, University of British Columbia, Vancouver, BC, in partial fulfillment of requirements for the Master of Science degree. The report sets guidelines for manganese (Mn) to protect aquatic life in the freshwater environment only. The Ministry of Environment, Lands and Parks (MELP) supported this work by providing (a) data on manganese toxicity relevant to aquatic organisms found in British Columbia and (b) professional guidance and review of the thesis report.

Table 1
Examples of the Recommended guidelines to Protect Freshwater Aquatic Life from Toxic Effects of Manganese.

Water use	Guideline (mg Total Mn/L)*
Maximum Concentration +	***Acute Guideline***
Water hardness	
25 mg/L $CaCO_3$	0.8
50 mg/L $CaCO_3$	1.1
100 mg/L $CaCO_3$	1.6
150 mg/L $CaCO_3$	2.2
300 mg/L $CaCO_3$	3.8
30-d Average Concentration ++	***Chronic Guideline***
Water hardness	
25 mg/L $CaCO_3$	0.7
50 mg/L $CaCO_3$	0.8
100 mg/L $CaCO_3$	1.0
150 mg/L $CaCO_3$	1.3
300 mg/L $CaCO_3$	1.9

* When ambient manganese concentration in the environment exceeds the guideline, then further degradation of the ambient or existing water quality should be avoided;
+ Instantaneous maximum calculated from: ≤ 0.01102 hardness + 0.54
++ Average of five weekly measurements took over a 30-day period. Calculated from: ≤ 0.0044 hardness + 0.605

Manganese guidelines were not set for agricultural (irrigation and livestock watering), wildlife and industrial water uses, since suitable data documenting the effects of manganese for these uses were not available in the literature. Appropriate documentation by Health Canada should be referred to for details on guidelines for the protection of drinking and recreational (e.g., swimming) water uses. Health Canada recommended an aesthetic objective of 0.05 mg/L manganese in drinking water to protect against staining (e.g., plumbing), but deemed unnecessary to provide guidance to protect from manganese toxicity in drinking and recreational waters.

Manganese, an essential trace element for aquatic and terrestrial biota, is only slightly to moderately toxic to aquatic organisms in excessive amounts. It is present in almost all organisms, and often ameliorates the hazard posed by other metals. Hence, most jurisdictions in the international arena have not promulgated manganese guidelines to protect freshwater and marine life. Nevertheless, manganese concentrations in the environment may be well above the aquatic toxicity levels in effluents originating from base and precious metal mines, municipal sewage and sludge, and landfills. A more detailed discussion on water quality guidelines for manganese is presented in the main body of the report.

Manganese preferentially binds to particulate matter. Typically, 90% to 95% of the total waterborne manganese residue is associated with the particulate matter. However, soluble species of the metal are considered to be the most toxic as they are readily available for biological reactions. It is, therefore, recommended that the proposed guidelines should be interpreted in terms of the dissolved metal fraction when the total manganese concentration in the environment exceeds the guideline due to particulate matter and adverse effects due to manganese are not obvious.

PREFACE

THE MINISTRY OF ENVIRONMENT, LANDS AND PARKS develops ambient water quality guidelines for British Columbia. This work has two goals:

- to provide guidance for the evaluation of data on water, sediment and biota, and
- to provide basis for setting site-specific ambient water quality objectives;

The guidelines represent safe conditions or safe levels of a substance in water. The term "guideline" is defined as "a maximum and/or a minimum value for a physical, chemical or biological characteristic of water, sediment or biota, which should not be exceeded to prevent detrimental effects from occurring to a water use under given environmental conditions."

Water Quality guidelines are applied province-wide, but they are use-specific, and are being developed for these water uses:

- raw drinking water, public water supply and food processing[1]
- aquatic life and wildlife
- agriculture (livestock watering and irrigation)
- recreation and aesthetics[2]
- industrial water supplies

The guidelines are established following a thorough review of the recent scientific literature, guidelines set by other jurisdictions, and environmental

[1] The guidelines apply to an ambient raw water source before it is diverted or treated for domestic use. The Ministry of Health regulates the quality of water for domestic use after it is treated and delivered by a water purveyor.

[2] Guidelines relating to public health at bathing beaches will be the same as those developed by the

conditions in British Columbia. The scientific literature provides information on environmental fate, persistence, and effects of toxicants on various life forms. This information is not always conclusive because it is often based on laboratory testing that, at best, only approximates field conditions. To compensate for this uncertainty, and applying the "precautionary principle", the guidelines have built-in safety factors that are conservative, while taking into account the natural background in the province.

The guidelines are used to set ambient site-specific water quality objectives for specific waterbodies. In setting the objectives, considerations are given to present and future water uses, waste discharges, hydrology, limnology, oceanography, and ambient water quality conditions at the site in question.

In most cases, the objectives are the same as the guidelines. However, when natural background levels of substances exceed the guidelines, the site-specific objective could be less stringent than the guideline in order to take this high natural level into account. In rare instances—for example, if the resource is unusually valuable or of special provincial or ecological significance—the safety factor could be increased enabling objectives to be more stringent than the guidelines. Another approach would be to develop site-specific objectives by conducting toxicity experiments in the field. However, because this approach is costly and time consuming, it is seldom used.

Neither the guidelines nor the objectives derived from them have any legal standing. However, objectives can be used to calculate waste discharge limits for contaminants. These limits are outlined in waste management

Ministry of Health, which regulates the recreation and aesthetic water use.

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permits, orders and approvals, all of which have legal standing. Objectives are not usually incorporated as conditions of a permit.

Water quality guidelines are subject to review and revision, as new information becomes available or as other circumstances dictate.

INTRODUCTION

MANGANESE IS AN ESSENTIAL ELEMENT in trace amounts for plants and animals. It forms an essential part of the enzyme systems that metabolise proteins and energy in all animals. It is also involved in the formation of mucopolysaccharides required for healthy joint membranes. In humans, manganese is involved in the digestion and absorption of food through peptidase activity, in the synthesis of cholesterol and fatty acids, in glucose metabolism, and in the use of biotin, thiamine, vitamin C and chlorine. In the divalent state (Mn^{++}), it appears to provide protection against oxygen free radicals as part of the enzyme superoxide dismutase. Insufficient dietary manganese may result in abnormal carbohydrate metabolism and impaired insulin productions in humans, and a host of ailments in experimental animals.

The primary concerns due to manganese in drinking water are its objectionable taste and its capacity to stain plumbing and laundry. In aquatic environments, manganese toxicity is slight to moderate and is influenced by several factors such as water hardness, salinity, pH, and the presence of other contaminants. The effect of water hardness on manganese toxicity is by far the most studied factor.

Manganese comprises approximately 0.085% to 0.95% of the earth's crust at an average concentration of 950 mg/kg. Principal ores of manganese include: pyrolusite (MnO_2), manganite ($Mn_2O_3 \bullet H_2O$), hausmannite (Mn_3O_4) and rhodocrosite ($MnCO_3$). Ferromanganese minerals such as biotite mica (K(mg,Fe)3(AlSi3O10)(OH)2) and amphibole ((Mg,Fe)Si8O22(OH)2) also contain large amounts of manganese. Manganese in rocks and minerals is naturally released into the environment from weathering.

Manganese and its compounds are frequently used in various industrial processes and consumer products, including:

- manufacturing of steel, and the production of alloys of steel, aluminum, and copper, where it neutralises the harmful effects of sulphur, serves as an anti-oxidant, and provides strength and toughness;
- as ingredient of alkaline batteries, electrical coils, ceramics, matches, welding rods, glass, dyes, paints, and drying industries;
- as dryers for paints, varnishes and oils, fertilisers, disinfectants, and animal foods; and
- as anti-knock compounds for internal combustion engines (e.g., a gasoline additive).

Total manganese concentrations in natural fresh waters seldom reach 1.0 mg/L and are usually less than 0.2 mg/L, while seawater typically contains about 0.002 mg/L manganese. The total concentration in fresh surface waters in BC was found to vary as follows: 0.01 - 1.7 mg Mn/L in the Coastal Region, 0.002 - 1.53 mg Mn/L in the Cariboo, Omineca, and the Peace Regions, and <0.001 - 0.56 mg Mn/L in the Thompson River region.

RECOMMENDED GUIDELINES

Aquatic Life

1. Freshwater: Chronic

To protect freshwater aquatic life from chronic effects, the average[3] concentration of total manganese in mg/L should not exceed the value as given by the following relationship:

Average Mn Concentration (mg/L) ≤ 0.0044 H + 0.605

In this relationship, the quantity H represents water hardness measured in units of mg/L as $CaCO_3$. The recommended guideline at a given hardness is based on the predicted value of manganese toxicity (obtained from the lowest observed effect concentration, or LOEC, and water hardness relationship) and an application factor of 0.25 (4:1 safety factor). The application factor of 0.25 was chosen instead of the more traditional factor of 0.1 (10:1 safety factor) due to the quality and amount of toxicity tests, and the range of species for which data were available. The results found in the literature suggested that the NOEC/IC25 ratio ranged from 0.6:1 and 1:1, where NOEC and IC25 represent the no observed effect concentration and the concentration at which a measurable biological response is anticipated in 25% of exposed organisms, respectively. Obviously, the factor of 0.25 will provide sufficient safety for the protection of aquatic life.

In the literature, the lowest chronic value was found to be 0.79 mg Mn/L. This value was a geometric mean of the lowest observed effect concentration (LOEC) of 1.04 mg Mn/L and the no observed effect

concentration (NOEC) of 0.60 mg Mn/L for rainbow trout exposed to the contaminant for four months in soft water (water hardness = 36.8 mg/L $CaCO_3$).

2 Freshwater: Acute

To protect freshwater aquatic life from acute and lethal effects, the maximum concentration of total manganese in mg/L at any time should not exceed the value as determined by the following relationship:

Maximum Mn Concentration (mg/L) ≤ 0.01102 H + 0.54

In the above relationship, the quantity H represents water hardness measured in units of mg/L as $CaCO_3$. The guidelines for the maximum concentration are based on the observed relationship between acute toxicity (96-h LC_{50}) of manganese and water hardness, and an application factor of 0.25 (safety factor of 4:1). The choice of the safety factor was based on the same factors as for the chronic guideline.

In the literature, the LOEC for acute effects (96-h LC50) was found to be 2.4 mg/L for coho exposed to manganese in soft water (water hardness = 25 mg/L $CaCO_3$). *Daphnia magna* also appeared to be acutely sensitive to manganese, showing a 48-h LC50 of 0.8 mg Mn/L. This adverse effect was, however, due to softness of the test water rather than the manganese concentration.

[3] Arithmetic mean is computed from five weekly samples collected over a 30-day period.

APPLICATION OF GUIDELINES FOR AQUATIC LIFE

MANGANESE is ubiquitous in the environment. Its impact on the environment depends upon several environmental factors including water hardness and ambient water quality conditions. Therefore, care must be exercised when the water quality guidelines are applied to assess environmental impacts of manganese.

1. ASSESSMENT OF EXISTING WATER QUALITY

Manganese shows variable behaviour in binding to particulate matter depending upon physical-chemical characteristics of the aquatic system. The literature shows that particulate manganese may account for more than 90% of the total waterborne residue. Furthermore, soluble forms of manganese are readily available for biological reactions and, therefore, are most toxic. It is, therefore, recommended that the manganese guidelines be interpreted in terms of the dissolved metal fraction when the total manganese concentration in the environment exceeds the guidelines due to the presence of particulate matter and adverse effects due to manganese are not obvious.

The water quality guidelines recommended in this document are primarily based on controlled, laboratory bioassays in which organisms were exposed to manganese alone. However, in the environment, manganese toxicity may be modified by many conditions, including water hardness. Other assessment techniques may be required to address manganese related issues in those situations (see below).

2. SETTING OF WATER QUALITY OBJECTIVES

In most cases, water quality objectives will be the same as the guidelines. When concentrations of manganese in undeveloped waterbodies are less than the recommended guidelines, then more stringent values, if justified, could apply. In some cases, socio-economic or other factors (e.g., higher background levels) may justify objectives that are less stringent than the guidelines. Site-specific impact studies would be required in such cases.

Manganese availability, and hence its toxicity, in the aquatic environment can be influenced by many factors, including water hardness. Although the literature alludes to this fact, there is a general lack of available research in this area. However, methods (e.g., water effects ratio, resident species toxicity in the field, etc.) are available to adapt the recommended guidelines to a given site by considering these. Where necessary, these methods can be employed to set site-specific water quality objectives. Because these approaches are costly and time consuming, they are seldom used.

In some instances, the ambient or existing concentrations of manganese in the environment may exceed the recommended guidelines. This may be evident especially in soft water environments. To protect aquatic life in such environments, it is recommended that degradation of the existing water quality should be avoided.

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